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Uses of alternative fuels and raw materials in the cement industry as sustainable waste management options

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ABSTRACT

The proper use of alternative fuels and materials in the cement industry is essential for the planning and promotion of different methods that can decrease the environmental impacts, lower the consumption of energy and material resources, and reduce the economic costs of this industry. Because of the great potential for the cement industry to save energy and reduce greenhouse gas emissions (GHG), many new research advances associated with the promising approach of introducing waste materials as alternative fuels or sustainable raw materials into the cement manufacturing process have been developed in recent years. Therefore, the main objective of this paper is to provide a literature review of these approaches based on previously published research studies. The analysis is specially focused on the technical, economic, and environmental effects of the uses of five solid wastes, namely, municipal solid waste (MSW), meat and bone animal meal (MBM), sewage sludge (SS), biomass, and end-of-life tyres (ELT), in the cement industry.

Contents

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1. Introduction

There is a great potential for the use of solid wastes as alternative fuels and raw materials in the cement manufacturing industry. From an energy consumption point of view, it is one of the most energy intensive consumers in the world. In particular, currently the data published in some studies reveal that the cement subsector accounts for approximately 10–15% of the total industrial energy use worldwide, which reached a consumption level of 120 kW h/t of cement [1,2]. Furthermore, cement plants are traditionally characterised as an intensive consumer of natural raw materials and fossil fuels, and as remarkable emitters of pollutants [3,4]. Cembureau [5] found that between 60 and 130 kg of fuel are fired per tonne of cement manufactured.

The cement industry sector released 2.37 Gt of total pollutants to the environment in 2000 [6]. Regarding carbon dioxide (CO_2) emissions, the cement industry generated approximately 1.8 Gt in 2005 [7] and, considering that the global emissions of CO_2 were approximately 28.3 Gt in 2005 [8], the cement industry contributed approximately 6% of the total global CO_2 emissions. However, in the last years this figure was reduced up to 5% in the worldwide or 4.1% in Europe considering the last improvements in energy efficiency and alternative fuels and materials [9].

Consequently, new scenarios and policies are being created as a result of the new trends in energy, environment, and waste legislations [10–14]. At the European level, the basic concepts and definitions regarding waste management were established by the waste framework directive 2008/98/EC [13], which also includes a "waste hierarchy" as one of the waste management principles used in waste policy decision making across the member states. Reducing the amount of waste generated is generally accepted as the main priority of the waste framework directive. However, other steps in the hierarchy, such as the reuse of products, the recycling of materials, other recovery processes (e.g., energy recovery), and the amount of disposal at landfills, are taken into account and are applied as part of different waste management strategies in different countries (as commented upon by Aranda et al. [15] and Vásquez et al. [16]).

In addition, the increase of energy efficiency and the reduction of greenhouse gas (GHG) emissions are also main objectives, as well as key factors in achieving long-term energy and climate goals. Since the inception of the European Climate Change Programme (ECCP I 2000–2004 and the on-going ECCP II) [17], a decisive emphasis has been placed on energy consumption, climate change, and energy efficiency improvements in Europe. In 2008, the ambitious objectives of reducing GHG emissions by 20%, increasing the share of renewable energy to 20%, and achieving a 20% improvement in energy efficiency by 2020 were established, although nowadays new analysis are performed to explore the options to move towards a 30% of reduction the main goal [18].

In this sense, the cement industry has a high potential to manage all of these tendencies as an integrated system to save energy, reduce GHG emissions, and recover waste materials [19,20]. To this end, the cement sector is presently focused on the diversification of energy sources, especially those used for waste treatment, and many factories can potentially use biomass or other material residues as energy-rich alternative fuels. Many of these alternative fuels are wastes or by-products from other industries. One of the best technologies for preventing the destruction of these materials in favour of their reuse is the use of these solid wastes as a supplementary fuel in cement kilns; hence, there are the simultaneous benefits of destroying these wastes while generating energy from them. Recovering the energy value of these wastes for cement production is a safe and valuable way of increasing energy recovery and material reuse [9,21,22]. Some options that are considered even include the use of waste materials as raw material substitutes in the clinker and the cement manufacturing process, providing significant savings in terms of natural resources, for example, up to 38% replacement of limestone or 72% replacement of clay [23,24].

Thus, this review is focused on promising approaches to simultaneously reduce the consumption of fossil fuel energy and natural resource materials via the introduction of the use of other waste materials into the cement industry. The main objective of this paper is to provide a literature review based on previously published research studies. The analysis also considers the technical, economic, and environmental effects of the uses of alternative fuels and raw materials in the cement industry. Particularly, the review analyses the most common wastes reused in the cement industry worldwide: municipal solid waste (MSW), meat and bone animal meal (MBM), sewage sludge (SS), biomass, and end-of-life tyres (ELT).

2. Overview of cement manufacturing

2.1. Worldwide production

One of the well-known characteristics of cement production is that cement plants are not uniformly distributed worldwide, and cement production depends on several social, economic, and geographical factors. According to the data of the European Cement Association [25], a total of 3.6 billion tonnes of cement were manufactured in the world in 2011, and more than half of this cement was produced by China (57.3%). The rest of the production is more evenly distributed among other important areas in Asiatic countries and Europe. Additionally, considering the evolution of the production of cement in the last decade, the amount of production in European countries has decreased, mainly because of the decline in the building sector as a result of the recent economic situation. However, in the case of developing countries from Asia and South America, the amount of production has slightly increased.

2.2. Description of the cement manufacturing process

As depicted in Fig. 1, cement production is a multistage process that involves different activities [26–29]. First, the raw meal is conditioned; the limestone and some additives containing calcium (Ca), silica (SiO_2), aluminium (Al), and iron oxides (Fe_2O_3) (among others) are crushed, ground, dried, and mixed. Then, this powder is heated in a pre-heater and pre-calciner (only in modern cement plants) to initiate the dissociation of carbonate $CaCO_3$ to calcium oxide (CaO) and CO_2. The powder is then burned in a kiln to continue the reaction between CaO and other elements to form

Nomenclature

BSE	Bovine spongiform encephalopathy
ELT	End-of-life tyres
GHG	Greenhouse gases
HHV	Higher heating value
IPCC	Intergovernmental panel on climate change
I-TEQ	International toxicity equivalent
LHV	Lower heating value
MBM	Meat and bone animal meal
MSW	Municipal solid waste
RDF	Refuse-derived fuel
SS	Sewage sludge
STP	Standard temperature and pressure
TDF	Tyre-derived fuel

Chemical compounds

Al_2O_3	Alumina
C_2H_4	Ethylene
CaO	Calcium oxide
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
CoO	Cobalt monoxide
Cr_2O_3	Chromium(III) oxide
Fe_2O_3	Iron oxide
H_2	Hydrogen
H_2O	Water
K_2O	Potassium oxide
K_2SO_4	Potassium sulphate
KCl	Potassium chloride
$MgCO_3$	Magnesium carbonate
MgO	Magnesium oxide
MnO	Manganese dioxide
Na_2O	Sodium oxide
NiO	Nickel oxide
P_2O_5	Phosphorus pentoxide
PAH	Polycyclic aromatic compounds
PbO	Lead oxide
PCB	Polychlorinated biphenyls
PCDD/F	Polychloro dibenzo-*p*-dioxin and polychloro dibenzofurans
SiO_2	Silica
SO_2	Sulphur dioxide
V_2O_5	Vanadium pentoxide
VOC	Volatile organic compounds
ZnO	Zinc oxide

calcium silicates and aluminates at temperatures of up to 1450 °C. The pre-calciner stage can process approximately 20–40% of the raw material before the kiln calcination step and, consequently, increase the energy efficiency of the kiln operation. Finally, the mixture that is obtained, called clinker, is cooled and subsequently ground with gypsum (approximately 5%) or other materials, such as slag, fly ash, pozzolans, or residues from other industries such as steel production materials [24,30], ceramics [23], or even construction and demolition materials [31]. The gypsum or other material is incorporated into the clinker to form the cement, which is ground again and packaged. Therefore, the burning zone of the kiln and the preheating and pre-calciner system (to which primary and secondary fuels are fed, respectively) are both heated to maintain the desired high temperature during the cement manufacturing process.

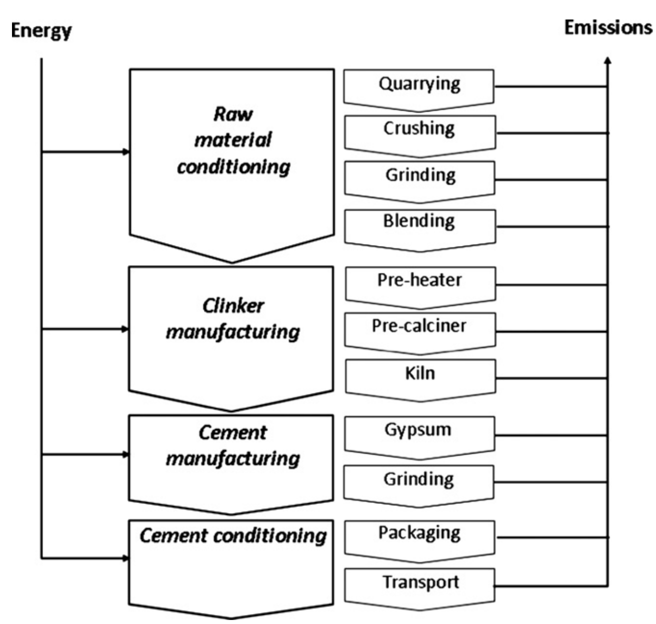


Fig. 1. Flow diagram of the cement manufacturing process, including the points of energy consumption and emissions.

Cement quality is an essential parameter to consider when alternative raw materials are introduced into the manufacturing process. The typical composition of clinker, which must be achieved in the mixture of natural raw materials and fuel ash, is shown in Table 1 [2]. Consequently, it is very important take the composition of the ash into account before the raw material powder is added to the kiln process to meet the desired quality requirements.

2.3. Energy consumption in the cement manufacturing process

An important component of the energy consumption during cement manufacturing that must be considered is the thermal energy consumption, which, from a theoretical point of view, can be considered to be approximately 1750 MJ to produce 1 t of Portland cement clinker [32,33]. However, Szabó et al. [34] found that the actual thermal energy requirement (3000–7000 MJ/t) is approximately 2–4 fold greater depending on the kiln technology used to burn the raw material. As evident in Table 2 and supported by the data of Szabó et al. [34] and Damtoft et al. [12], dry manufacturing processes result in energy savings, whereas the energy consumption is higher for the wet process, in which the raw material is fed into the kiln in the form of a slurry, because the energy required for the water evaporation process. Moreover, the use of other elements, such as pre-heaters

Table 1
Composition of cement produced by the dry manufacturing process. Data obtained from [2].

Compound	Composition (%)
CaO	65 ± 3
SiO_2	21 ± 2
Al_2O_3	5 ± 1.5
FeO_3	3 ± 1

and pre-calciners, can contribute to energy savings in the manufacturing process [35]. In this sense, a special attention is focused in the design and optimization of calciners as is demonstrated by Mikulčić et al. [36].

On the contrary, Madlool et al. [2] reported an average electrical energy distribution for the cement industry, which is shown in Table 3. The electrical power consumption associated with the production of cement is approximately 270 MJ/t of cement. The higher-energy consumers are those devices related to the kiln feed, the cooler, and the cement grinding and transport processes, which account for more than 50% of the total electrical energy consumption.

Table 2
Ranges in the thermal energy consumption and quantification of the fuel-derived CO_2 released (from traditional fuels) per tonne of clinker depending on the type of kiln technology. Data obtained from [12,34].

Kiln technology	MJ/t of clinker	kg fuel-derived CO_2/kg of clinker
Dry rotary kiln with pre-heater and pre-calciner	3000–4000	0.31–0.38
Dry rotary kiln with pre-heater	3100–4200	
Dry long rotary kiln	Up to 5000	0.4–0.6
Semi-dry rotary kiln	3400–4000	
Wet rotary kiln	5000–7500	
Shaft kiln	3100–6500 and higher	No data found

Table 3
Electrical energy distribution in the cement industry. Data obtained from [2].

Section/equipment	Electrical energy consumption (kW h/t)	Share (%)
Mines, crusher and stacking	1.50	2.00
Re-claimer, raw material grinding and transport	18.00	24.00
Kiln feed, kiln and cooler	22.00	29.30
Coal mill	5.00	6.70
Cement grinding and transport	23.00	30.70
Packing	1.50	2.00
Lighting, pumps and services	4.00	5.30
Total	75.00	100.00

2.4. CO_2 emissions from the cement industry

Two major sources of CO_2 emissions can be identified in the cement industry. The first source is linked to the energy used for the fuel combustion for burning the clinker, and running the pre-heaters and other operations. The second source is the natural release of CO_2 associated with the de-carbonation of limestone to produce the calcium silicates and aluminates in the clinker processes under intense heat [3,6,32,35,37].

However, there are other minor sources that should also be considered [38]. As illustrated in Fig. 2 by Habert et al. [39], lower amounts of CO_2 emissions are also produced by several stages, such as the quarrying of raw materials and their transportation, grinding, and packing, among others.

2.4.1. The raw material calcination process and cement production

The calcination process can be expressed by the reaction [40],

$$XCO_3 + heat \rightarrow XO + CO_2$$

where X usually refers to Ca and Mg. Therefore, the $MgCO_3$ and $CaCO_3$ are converted into CaO or MgO, respectively, the main components of the clinker. In the XCO_3-firing process, large amounts of CO_2 are released into the atmosphere, the amount of which is essentially directly proportional to the XO content of the clinker. van Oss et al. [41] reported that approximately 65% of the clinker is CaO or MgO. Additionally, according to Hendriks et al. [32], the amount of CO_2 emissions depends on another factor related to the final cement production called the clinker/cement ratio, which normally varies from 0.50 to 0.95. Decreasing the clinker/cement ratio is expected to reduce the emissions per tonne of cement. Taking these conditions into account, an average of 0.50–0.53 kg of CO_2 is considered to be produced per kg clinker [12,32,41].

2.4.2. Combustion of traditional fuels

Traditionally, fossil fuels such as coal, fuel oil, petroleum coke, natural gas, or diesel are used in the cement industry in the kilns and the pre-heater system to produce the high temperatures necessary for the formation of the clinker. The World Business Council for Sustainable Development [38] stated that approximately 40% of the GHG released during the cement manufacturing process are generated in this stage.

However, the quantification of the CO_2 emissions from fossil fuel combustion is more difficult and inaccurate than that from the de-carbonation process. In this case, the emissions from fossil

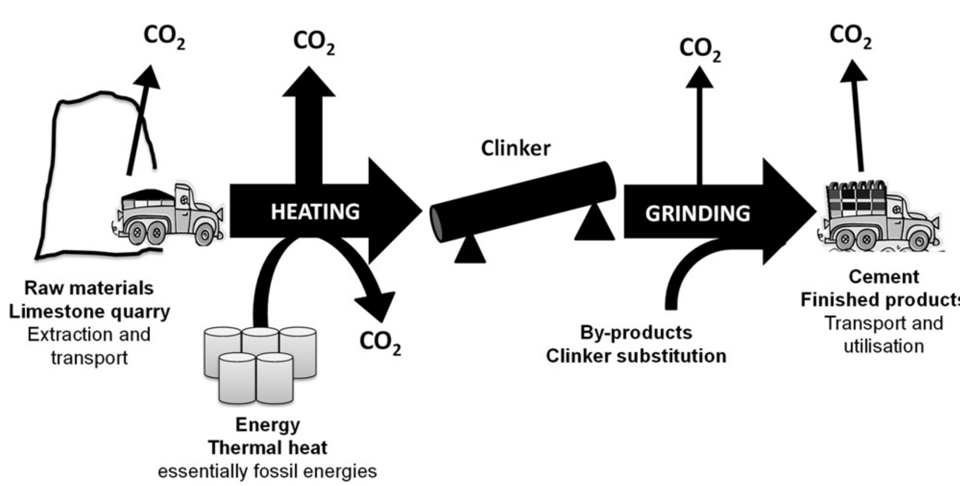


Fig. 2. Simplified cement fabrication process and associated CO_2 emission sources, and their relative magnitudes (denoted by the widths of the arrows). Data obtained from [39].

Table 4
CO_2 emissions per GJ of energy for several traditional fuels. Data obtained from [4].

Fuel	kt of CO_2/GJ
Petroleum coke	97.5
Coal	94.6
Fuel oil	77.4
Natural gas	56.1

fuel combustion are dependent on the types and quantities of the actual fuels burned, together with their interrelated carbon and heat factors (contents), as well as the kiln technology used for the burning process [41].

Table 2 shows the different ranges of fuel-derived CO_2 emissions per kg of clinker. Modern technologies based on the use of a dry rotary kiln with a pre-heater and pre-calciner have low emission ratios of approximately 0.31 kg CO_2 per kg of clinker, while other less efficient systems and conditions, such as those for the use of a wet rotary kiln without pre-heaters or pre-calciners, can produce approximately 0.6 kg CO_2 per kg of clinker [12,34].

On the contrary, the type of traditional fuel used also has a large impact on the CO_2 emissions because of the differences in their compositions. As depicted in Table 4, petcoke has one of the highest GHG emission ratios, releasing almost 98 kt of CO_2 per GJ of energy produced. Coal is also a high CO_2 emitter, as opposed to natural gas, which produces 56.1 kt of CO_2 per GJ of energy. Despite this lower emission ratio, natural gas is not used very extensively in the cement industry [4].

3. Technical, environmental, and economic considerations and challenges

3.1. Types of alternative fuels and raw materials at European framework

As mentioned above, approximately 50% of the total CO_2 emissions from the cement manufacturing process are released by the chemical processes and approximately 40% are released from burning fuel. A minor contribution, 10%, is derived from electricity use or transport processes [38]. Although it is more difficult to decrease the emissions related to the calcination process, some progress are achieved in this sense by replacing the limestone or clay component, and thus saving natural resources. However, there is a great deal of promise for lowering the emissions associated with the combustion process and reducing fossil fuel consumption without decreasing the quality of the final product. Therefore, the net emissions of GHGs can be reduced replacing fossil fuels with alternative fuels and reducing the use of natural materials.

This process consists basically of replacing a portion of the traditional fuel and natural raw material used with alternative waste resources. The introduction of alternative wastes depends on the composition and type of these materials, and the final mixture with traditional fuels and original raw meals, requiring, in some cases, modifications of the manufacturing equipment or the intermediary processes if there is complete or very high of substitution of fuel with alternative wastes [42]. Regardless of the degree of substitution, cement plants offer a very suitable opportunity for the replacement of traditional fuel and natural raw materials with alternative waste resources. The main conditions of the production process will allow the exploitation of various types of waste energy with suitable technical and environmental practices.

Table 5
Replacement ratios of fossil fuels with waste materials in selected European countries, 2010–2011. Data obtained from [43].

Country	Replacement ratio (%)	Country	Replacement ratio (%)
Italy	8.6	Austria	63.1
Spain	22.4	Switzerland	49.0
Denmark	25.0	Belgium	47.3
France	29.4	Germany	62.0
Sweden	29.0	Netherlands	83.0
Norway	60.0	United Kingdom	39.5
Average UE-27 (2010)	30.5		

In 2011, Europe produced 201 million tonnes of cement, which is equivalent to an investment of 33.2 million tonnes of raw materials. Additionally, about 0.8 million tonnes of wastes materials were used, and consequently 22.4% of the energy consumption could be saved [43]. According to Seboka et al. [44], it is estimated that, in case of biomass, one litre of fuel oil can be replaced by 3–4 kg of biomass used in direct combustion or more than 4 kg in the case of gasification.

The use of waste materials in European cement plants has been widely extended in recent years. Nowadays, the European Union contained 268 cement plants, and more than 64% of the facilities use waste materials as alternative fuels [45].

However, the degree of alternative fuel use differs depending on the country. Table 5 shows the replacement ratios of fossil fuels by alternative fuels between 2010 and 2011 for a number of European countries [43]. As shown, the highest ratio (83%) belonged to Netherlands, but several countries achieved significant replacement ratios, such as Austria, Germany and Norway about 60–63% or Switzerland and Belgium from 47 to 49%. On the other hand, although Italy and Spain have only achieved low replacement ratios, approximately 8.6 and 22.4%, respectively, these countries have increased their volume of alternative fuel substitution in recent years. In the case of Spain, the use of alternative fuels increased about 22% compared with 2004, when approximately 175.000 t of wastes materials were recovery material o energetically. These finding demonstrate the high unrealised potential that alternative fuels still have in the cement industry. Additionally, in 2009, the Portland Cement Association [46] estimated that, in the United States, many plants met 20–70% of their energy requirements with alternative fuels.

A wide range of alternative fuels are used, and these fuels can be classified into three basic groups [47]: gas (e.g., landfill gas, pyrolytic gas, and biogas), liquid (e.g., used oils and solvents), and solid (tyres, wood waste, plastics, MBM, municipal waste, SS, and textiles).

Fig. 3 shows the replacement ratio for each type of alternative fuel in each country. According to this figure, MBM and SS are the alternative fuels most widely used in the cement industry. These two fuels are used in almost all the countries examined, as are tyres (but in lower quantities). Despite the fact that most of the countries use a wide array of alternative fuels, the case of the Netherlands is remarkable. This country is especially focused on the recovery of energy from SS (42.2% replacement ratio), although other alternative fuels such as MBM, plastics, and solvents are also used. In spite of the large impact of refuse-derived fuel (RDF) on the waste management chain, the use of RDFs is not taken account in this figure. However, RDF use is analysed in following sections [48].

Some criteria for the use of these materials are expected to fulfil certain technical or legislative requirements. Most of these materials are regulated to ensure environmental protection. The

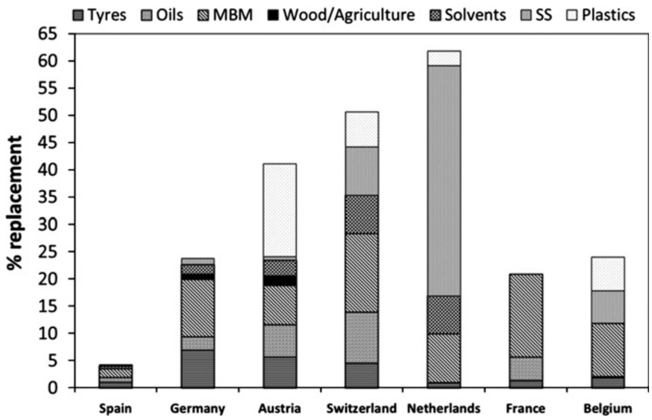


Fig. 3. Ratio of replacement regarding the type of alternative fuel by country. Data obtained from [48].

Table 6
Recommended composition of fuels for the cement industry. Data obtained from [49].

Component	Value
Chlorine	< 0.2%
Sulphur	< 2.5%
PCB	< 50 ppm
Heavy metals (excluding Hg, Cd and Tll)	< 2500 ppm
Hg	< 10 ppm
Cd + Tl	< 90 ppm

most important aspects to take into account in terms of European legislative considerations are summarised in Table 6. Specific restrictions exist for some components such as chlorines and sulphur [49]. Some authors, e.g., Enders and Haeseli [50], noticed that these substances can cause problems in cement plants, for instance, pre-heater clogging as a result of condensation and volatilisation reactions and, hence, instabilities in the kiln process. In particular, chlorine exerts the most harmful effects on the cement manufacturing systems. Additionally, the contents of polychlorinated biphenyl (PCB) and metals are also important considerations. Although some studies demonstrate the suitability and harmlessness of burning PCB substances in a cement kiln [51], some restrictions are already mandated. The combustion of the clinker is well suited for the use of various alternative fuels because of the long residence times in both the rotary kiln and the gas channels, and the high temperatures achieved.

On the other hand, technical criteria are also established by some authors, such as Madlool et al. and Mokrzycki et al. [2,47], and these criteria are related to the following material characteristics:

- Physical state of the alternative fuels. Gaseous fuels have the advantage that they are more homogenous in composition.
- Calorific value over 14 MJ/kg. For instance, some alternative fuels have values that are usually between 18 and 25 MJ/kg [52].
- Physical properties such as the scrap size, density, or homogeneity.
- Grinding properties.
- Moisture content. Normally, a water content below 20% is required.
- Compatibility with the current technology or accessible technical changes.
- The cement quality must not be affected.
- The cost of the alternative fuel should be lower than that of traditional fuels.

As evident from the list above, among other important considerations, an appropriate and homogeneous chemical composition is essential and depends on the type of component and the organic and inorganic contents. Moreover, the energy content and the ash content as well as the moisture content and volatile compounds present are also important. However, in most cases, alternative fuels are made up of mixtures of different waste materials, and it is difficult to determine their energy value or composition.

Specifically, materials like municipal wastes, oils, plastics, wood, tyres, or sludges are often proposed as alternative fuels for the cement industry. These materials are selected based on their price and availability.

In Table 7, the composition and properties of the most common alternative fuels (coal and petcoke) and several alternative fuels are listed (data from studies developed by Kääntee et al. [27] and completed by Lopes et al. [53]). The waste materials, especially biomass or agriculture residues, have a higher ash content than the traditional fuels, with ash defined as the mineral content in the fuel that remains in an oxidised form after complete combustion. On the other hand, RDF is a very heterogeneous mixture and has different physical and chemical properties depending on the source. For this reason, it is not included in Table 7 and is analysed in Section 5.

3.2. Impact of the introduction of waste materials into the cement manufacturing process

3.2.1. Direct effects on the manufacturing process and the quality of the product

Clearly, the substitution of alternative raw materials can directly modify the quality of the cement produced; therefore, the composition of the new raw material must be considered before it is used as a substitute. However, Bolwerk et al. [52] established that the cement production process can also be affected by the choice of the point at which the material is fed into the rotary kiln. Normally, the fuel can be introduced to the kiln at the following points:

- At the main burner.
- At the transition chamber of the rotary kiln.
- At the riser pipe through the secondary fuel burners.
- At the pre-calciner through the pre-calciner burners.
- At the pre-calciner in the large pieces of fuel feed.

In addition, alternative fuels have different properties than traditional fuels. Normally, alternative fuels have higher material densities and transport characteristics, and these factors have a large influence on the burning process. High replacement ratios result in large alterations to the burning process. The main characteristics of the burning process that are affected are related to the temperature profile of the kiln, including the sintering temperature, the length of the burning zone, and the cooling conditions. Subsequently, the characteristics of the clinker, such as the burning grade, the granulometry, and the degree of crystallisation, can be drastically altered [19].

However, it is demonstrated that is possible to maintain the correct kiln temperature profile, especially in the case of material feeding introduced at the raw material section or by the burner end of the kiln, by controlling the feeding system and the fuel homogeneity with alternative materials with a uniform heating value and moisture content. These characteristics can be achieved

Table 7
Composition of several fuel used in the cement industry. Data obtained from [27,53].

Dry, in wt% (unless otherwise indicated)	Bitumi-nous coal	Petcoke	MBM	SS	Car tyre scrap (average)	Car tyre rubber	Agriculture biomass (average)
LHV (MJ/kg)	27.4	33.7	16.2	15.8	35.5	35.6	17.97
HHV (MJ/kg)	28.4					37.3	
C-fix	53.0	89.5	7.20	5.00	30.6	31.1	16.3
Ash	11.1	0.50	28.3	17.9	6.35	2.20	4.2
Volatiles	35.9	10.0	64.5	85.0	69.4	66.6	79.47
H_2O	3.0	1.50	8.09	5.20	0.66	0.73	7.6
C	70.6	89.5	42.1	40.5	79.6	87.0	48.73
H	4.3	3.08	5.83	7.0	7.0	7.82	5.9
N	1.2	1.71	7.52	0.84	0.43	0.33	0.6
S	1.3	4.00	0.38	0.12	1.54	0.80	0.08
O	11.8	1.11	15.3	25.2	5.0	1.81	
Cl	0.07		0.20	1.0	0.063		0.2
Ash analysis							
P_2O_5	0.016		41.2		0.015		5.09
Na_2O	0.05		1.47		0.04	0.9	1.21
K_2O	0.12		0.28		0.038	1.1	38.55
CaO	0.18		18.4	1.83	0.53	8.7	19.74
Fe_2O_3	0.31		0.14		0.36	1.7	1.27
Al_2O_3	1.07		0.02		0.11	16.6	1.59
SiO_2	2.0		0.45		0.94	27.8	26.81
Heavy metal							
MgO	0.08			0.32		1.2	5.76
NiO		0.0432			0.018	0.0065	
Hg (mg/kg)		0.05			$<$ 0.1		
PbO		0.00053			0.004	0.0373	
ZnO		0.00103			1.48	56.6	
MnO						0.021	
V_2O_5		0.0906				0.0043	
As (mg/kg)		0.7					
Cr_2O_3				0.0013	0.034	0.0008	
Cd (mg/kg)		0.46			8		
CoO		0.0001				0.495	

more easily if the waste materials are previously gasified and the alternative fuels are introduced into the kiln as a rich energy-producing gas. In this case, the composition is uniform and some of the previously described problems can be avoided.

Moreover, the amount and nature of the fuel ash is very important. Normally, the ash produced in the burning process can be added as a raw material, but the content of ash in the fuel composition can limit the quantity of ash from the combustion process that can be reused. If the ash composition is not maintained in a suitable range, the quality of the final product can be altered significantly [44].

Carpio et al. [54] developed a model that predicts the raw composition of the clinker when alternative fuels are used directly as secondary fuels in cement rotary kilns. The model also calculates the substitution levels of the primary fuel by the alternative fuel derived from industrial wastes that are considered acceptable in terms of the pollutant emission levels (sulphur or phosphorous for example). Based on the presented results, the performance of the model is shown to be satisfactory for both maintaining the values of the chemical composition of the clinker within the quality parameters and reducing production costs.

The air supply needed for combustion is another important parameter to take into account if the introduction of alternative raw materials presents limitations to the air supply unit. If the air requirements are high, the kiln fans must run at high speed, consequently increasing the exhaust gas flow, which can affect the whole function of the pre-heating system. On the other hand, if there is a decrease in the air requirements, extra capacity on the fan side is acquired, providing the opportunity to increase production levels. These facts are also very important considerations for maintaining the quality of the product; therefore, the conditions in the kiln system must be carefully controlled.

If the alternative fuels are previously treated by gasification, the air quantities related only to this process also have great importance. Seventy-nine percent of air is nitrogen, which is an inert gas that dilutes the gas produced by the gasification process, decreasing the energy value of this gas. Therefore, most gasifiers are designed to use only oxygen and to optimise the amount of oxygen fed into the system to produce gases with a high energy content per unit volume.

In this regard, Kääntee et al. [27] developed a model under the ASPEN platform to simulate the combustion requirements for different alternative fuels in compression with petcoke. In the cases of MBM or SS fed into the raiser, the results demonstrate that a slightly higher amount of air (3–4%) must be supplied when operating the gasifier with larger amounts of alternative fuel. Although air requirements are quite similar, problems may arise, especially when setting the operational values for the gasification process (the fan speed, production levels, and dust emissions), that cannot be overcome by the air supply unit. In the case when these same alternative fuels are fed directly into the burning zone, the air requirements increase by up to 10%. However, when the ratio of alternative fuel to petcoke is lowered, the additional air requirements are minor.

3.2.2. Economic effects

The investment costs are strongly linked to the cement plant technology. According to Barker et al. [7], conventional facilities (dry processing with a 5-stage pre-heater and a pre-calciner) cost approximately 263 million euros, while including other processes for CO_2 capture and storage can raise the cost to 558 million euros when post combustion processes are used. However, when a cement plant is built and the investment costs are fixed, only the operational and maintenance costs can be modified.

Nevertheless, clinker production is an intensive energy-consuming process that accounts for between 20 and 40% of the total cost of cement manufacturing. Taking into account that 3.3 GJ of energy, on average, are required to produce 1 t of cement [34,49] in conventional plants and at traditional fuels prices (e.g., 2.51 euros/GJ and 2.34 euros/GJ for coal and petcoke, respectively), approximately 8 euros per tonne of cement is required. Moreover, this value can increase sharply up to 21.5 euros per tonne of cement when post combustion technologies are included [7]. However, wastes are less expensive than traditional fuels or even free. Therefore, a reduction of fuel costs currently offers the best opportunity for cost saving in the industry. A similar situation exists for the case of using alternative raw materials in the cement process.

Thus, the replacement of quantities of traditional resources with alternative resources decreases the costs of raw materials. For example, a conventional plant with an annual production of 1 million of tonnes and a fuel replacement ratio of 30% with free alternative fuel could save up to 2.4 million. This savings is an important issue because, other fixed costs, such as the cost of electricity, remain beyond the control of manufacturers and have even increased in recent years. Hence, raw materials and fuels are indeed the only component for which the costs can be reduced. Additionally, biomass CO_2 emissions do not count against global CO_2 emissions, and therefore, biomass CO_2 emissions are excluded from the Emission Trading System in the European Union policy [55]. This fact is especially important from 2012 onwards, when the lion's share of carbon allowances will not be allocated for free, and industry will have to pay more for their pollutant gas emissions.

On the other hand, the recovery of energy and materials for their reuse is completely in accordance with the European Union policy established by Directive 2008/98/EC [13], in which a waste hierarchy was established to reduce the disposal of waste materials in landfills or by incineration. This waste reduction will lead to a reduced number of new disposal sites, a limitation of the expansion of existing sites, and will reduce the necessity to build incineration plants. This waste reduction also produces cost savings for the overall energy system.

Additionally, substitutions of alternative fuels and raw materials are powerful alternatives to the use of traditional fuels in non-producer countries or developing countries that want to implement independent, integrated waste management, and fuel supply systems for the cement industry and provide energy security against volatile global energy markets [44].

3.2.3. Environmental effects

The net emissions of GHGs can be reduced drastically by replacing traditional fuels with other materials such as agricultural biomass, MSW, or MBM. The main reason is that the carbon contained in alternative fuels is considered carbon-neutral. However, some alternative fuels, such as plastics, oils, or used tyres, are not entirely approved as carbon-neutral by the intergovernmental panel on climate change (IPCC) [56], although the impacts of these fuels are lower than those of traditional fuels as shown in Table 8.

However, the use of any of these alternative fuels, not only the carbon-neutral fuels, for cement production results in a significant net reduction in CO_2 emissions because cement kilns are more efficient in comparison with other common incinerators. Karstensen et al. [57] noted that the combustion conditions in cement kilns are perfect for the use of alternative fuels made from waste or treated hazardous waste. The most important conditions are the high temperatures, long residence time, surplus oxygen concentrations during and after combustion, good turbulence and mixing conditions, thermal inertia, dry scrubbing of the exit gas by alkaline raw materials, fixation of the trace heavy metals in the clinker structure, lack of generation of by-products such as slag, ashes, or liquid residues and complete recovery of energy, and raw material components in the waste.

Table 8
Energy efficiency of cement fuels. Data obtained from [39].

Fuel net CO_2 emissions factor	(g_{CO_2}/MJ)
Petcoke	101
Coal	96
Natural gas	54.2
Used tyres	85
Plastic	75
Waste oil	74
Refused derived fuels	8.7
Animal meal	0
Waste wood	0

To foster complete combustion, especially of high molecular weight hydrocarbons, high kiln temperatures, and adequate residence times are required. Therefore, the clinkering zone temperature is higher than 1427 °C and the flame temperatures are approximately 1627–1827 °C, while gas flow velocities from 12.1 to 13.5 m/s result in residence times of approximately 2.7 s when the temperature is above 1397 °C. Lower temperatures are associated with an increase in the residence time up to 5.0 s at 1197 °C [49]. The temperature and residence time are especially important in the case of dioxin and furan (PCDD/Fs) emissions, especially those from animal waste. While the maximum quantities of these substances are detected at 700 and 800 °C, cement combustion conditions produce minimal amounts of emissions of these compounds. Presently, cement kilns can achieve an emission level of 0.1 ng I-TEQ/m^3. Hence, the proper replacement of fossil fuels by wastes, even hazardous materials, is not a significant problem in terms of the formation of PCDD/Fs [57,58].

Another advantage of cement production is that the process of fuel combustion in rotary cement furnaces is a non-waste process because no residues are generated as the ashes can be incorporated into the clinker.

Additionally, the alkaline environment is an important feature that contributes to the favourability of the use of cement kilns for alternative fuel applications. This basic environment contributes to the neutralisation and capture of acid gas components produced by combustion. Furthermore, heavy metals condense on dust molecules and are returned back to the clinker [49].

4. Best available routes to use solid wastes in the cement industry

Different technical options are available to use waste materials in cement factories, as depicted in Fig. 4. Waste materials can be introduced directly into the kiln as alternative fuels and raw materials. On the other hand, waste can be treated by gasification or incineration processes beforehand. In these cases, the by-products of these stages, such as the gas produced from gasification or the ashes generated by incineration, can also be used as fuel or raw materials in the cement industry.

4.1. Direct combustion

Direct combustion is a well-known method and has been traditionally used in recent years. The pyro-processing system offers the chance to reduce energy consumption and decrease the

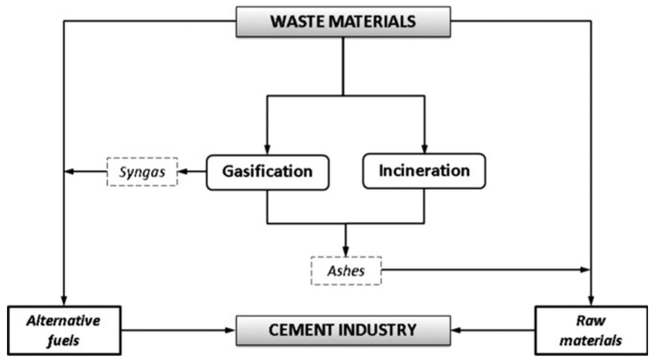


Fig. 4. Summary of available technical options to use alternative fuels.

emissions associated with the direct combustion of alternative fuels in the pre-heater and pre-calciner systems, where more than 60% of the energy input is used and 80–90% of the calcination process occurs. Moreover, lower temperatures reduce the nitrogen oxide (NO_x) emissions [2].

In systems with pre-calciners, the quality of the fuel is less restrictive and the kiln performance and clinker quality are less affected by the fuel quality. However, in a conventional pre-heater kiln (i.e., without a pre-calciner), it is only possible to burn mixtures with proportions of alternative fuels up to 30%, and there are some limitations in the fuel conditions. The remainder of the fuel energy is burned into the kiln chamber [19].

On the contrary, direct combustion requires pre-conditioning processes before the use of alternative fuels (cleaning, drying, and homogenising) to achieve uniform heating values and the pre-processing units have to be integrated into the plant.

In the case of direct combustion in the kiln, for which mainly vertical kilns (shaft kilns) and rotary kilns are used [29], especially rotary kilns, any fuel feeding phase or condition can be used. However, vertical shaft kilns are only suitable for the use of pulverised mixtures with petcoke, liquid, or gases.

As described above, the high temperatures and long retention times in the kilns offer high levels of energy-efficiency and allow for complete combustion, minimising the emissions of non-combusted pollutants.

4.2. Gasification

The gasification process of alternative fuels is based on the generation of a rich energy producer gas that consists of a mixture of hydrogen (H_2), carbon monoxide (CO), CO_2, water vapour, and methane (CH_4), also called 'synthesis gas' or 'syngas'. This syngas is then co-fired in the kilns, pre-heaters, and pre-calciners using a gas burner. On average, approximately 2.5 m^3 of syngas at standard conditions (STP) are generated from 1 kg of biomass [59]. This technology can be applied to a wide variety of fuels and is not greatly affected by the fuel composition because of the high level of homogeneity in the final gas. Therefore, the gasification of MSW is particularly convenient because of its initial heterogeneity.

Normally, the technology applied to syngas production from alternative fuels consists of using circulating fluidised bed gasifiers in the case of conventional gasification systems, or plasma gasifiers in the case of high-temperature gasification.

The most widely used gasification technology for industrial-scale applications is the fluidised bed gasifier. The benefits of fluidised bed gasifiers, especially the remarkably good temperature control (800–850 °C), high reaction rates, high carbon conversion ratio (approaching 100% within the bed), and high quality of the gas produced, were noted by Cioni et al. [60]. However, the main disadvantage is that fluidised bed gasifiers typically enhance the drag of the fine particles produced from the elutriation of ash and fuel, which enriches the gas with solids that must be removed, as reported by Seboka et al. [44].

In addition, recent research [61–63] indicate that plasma gasifiers have become one of the most promising technical and environmental alternatives for solid waste treatment and energy utilisation. This technology generates intense heat to initiate and supplement the gasification reactions, heating the feedstock to more than 2000 °C, and in comparison with combustion process, the quantity of oxidising agents (air, oxygen, steam, or a mixture) required is lower and a syngas with a higher H_2 content is obtained. Because of the high temperatures, organic compounds are dissociated into very simple molecules and even hazardous wastes are transformed into a useful syngas. Inorganic materials (mainly oxides) are melted, fused, and vitrified into a type of glass called slag that is extremely stable and inert. This slag is non-hazardous and can be used in the cement process as a raw material.

Conventional gasification, in which the temperature is lower, produces incomplete reactions, and hence, large quantities of slag and ash are generated, and less syngas is produced.

5. Review of selected alternative fuels

There is a wide variety of alternative fuels. However, this review focuses mainly on the most widely used materials, especially because of waste management considerations such as those for MBM, MSW, ELT, and SS. Additionally, the use of biomass in the form of wood or agriculture residues is also reviewed in this study.

5.1. Animal meat and bone meat (MBM)

MBM waste management became problematic when bovine spongiform encephalopathy (BSE) was discovered. As a result, the use of MBM residues in animal feed or landfilling was forbidden. Finally, thermal treatment, by incineration or gasification, became available as an alternative because the potential BSE pathogens are destroyed in high-temperature processes, especially those with long residence times and adequate oxygen supplies. To improve the waste management hierarchy, the energy recovery by means of the use of MBM in cement plants has been widely considered [64].

However, it is demonstrated that the continuous feeding of MBM into a fluidised bed reactor or combustor could generate significant agglomerations in the feeding system due to the high fat content of MBM [65]. Therefore, most studies have analysed the behaviour of MBM as an alternative fuel in different processes: the co-combustion of MBM with coal [66,67], pyrolysis [58], and co-gasification [68] including a fixed bed reactor and a fluidised bed reactor. The producer gas from gasification is energy rich and can be easily used as a fuel in other processes.

Gulyurtlu et al. [66] performed several tests with different MBM/coal ratios to determine the influence of various MBM parameters on the process of co-combustion with coal. This research demonstrates that minor impacts on emissions, particularly those of CO and sulphur dioxide (SO_2), are evident when the ratio of MBM is increased, as shown in Table 9. In the case of the decrease in SO_2 emissions, the main factor is the Ca contained in the MBM; the Ca can capture sulphur in a solid phase. However, the use of MBM could increase NO_x emissions because of the high nitrogen content in MBM.

Table 9
Concentrations of compounds in gas emissions after the co-combustion of MBM and coal. Data obtained from [66].

Parameter	Units	100% MBM	50% MBM	20% MBM	100% coal
CO	mg/N/m^3 (11%O_2)	8	165	281	270
N_2O	mg/N/m^3 (11%O_2)	37	115	139	86
NO_x	mg/N/m^3 (11%O_2)	398	273	201	259
SO_2	mg/N/m^3 (11%O_2)	14	321	502	713
VOCs	mg/N/m^3 (11%O_2)	10	4	6	2

Table 10
Summary of the results obtained for compounds in the emissions from the stack. Data obtained from [66].

Parameters	Units	100% MBM	50% MBM	20% MBM	100% coal
O_2	%vol	12.5	9.5	7	9
CO_2	%vol	8.2	10.7	11.6	12.2
Moisture in gases	%vol	4.71	4.63	4.66	4.68
Molecular mass	g/mol	29.26	29.25	30.37	28.68
Gas temperature	°C	157	152	159	110
Stack gas velocity	m/s	2.44	2.39	2.52	2.16
Dry gas flow rate	N/m^3/h	184	183	190	183
Fly ash particles	mg/N/m^3 (11%O_2)	392	88	118	122
Cl^-	mg/Nm^3 (11%O_2)	210	93	40	8
F^-	mg/N/m^3 (11%O_2)	< LQ	< LQ	< LQ	< LQ
Cd	mg/N/m^3 (11%O_2)	0.001	0.001	0	0.002
Cr	mg/N/m^3 (11%O_2)	0.547	0.093	0.115	0.024
Cu	mg/N/m^3 (11%O_2)	0.068	0.038	0.026	0.025
Ni	mg/N/m^3 (11%O_2)	0.013	0.11	0.062	0.017
Pb	mg/Nm^3 (11%O_2)	0.069	0.059	0.022	0.016
Mn	mg/Nm^3 (11%O_2)	0.004	0.029	0.026	0.025
As	mg/N/m^3 (11%O_2)	0.051	0.072	0.048	0.056

Additionally, it was determined that the combustion process produces less leachable and toxic ashes than the parent MBM, results were also supported by the findings of Cyr and Ludmann [69]. Another important aspect of MBM is related to the proteins contained in the animal meal. In this case, the emissions that might be released to the environment are destroyed.

On the other hand, in case of MBM co-combusted with coal, Fryda et al. [67] reported that the Al and Ca contained in the ash inhibits severe agglomeration by preventing the formation of alkali silicates that melt at low temperatures.

A summary of the emissions obtained from the stack is listed in Table 10 [66].

In co-combustion, depending on the type of secondary fuel, the management of the feeding behaviour and the maintenance of the dosage are complex. Therefore, a thermal pre-treatment of the secondary fuel, such as gasification, may help to achieve homogenisation before supplying this fuel to the cement manufacturing process.

The gasification or co-gasification of MBM could be a feasible alternative to MBM co-combustion. Cascarosa et al. [68] researched the co-gasification of low percentages of MBM with coal (up to 1%) in a fluidised bed reactor to evaluate co-gasification (800–900 °C) as a potential waste management alternative. The results show that substituting 1 wt% of the coal used in this gasification process with MBM slightly increases the amounts of both gas and tar and notably decreases the yield of char.

The gas composition barely changes in response to the addition of 1 wt% MBM, as illustrated in Fig. 5, although the results show that increasing the MBM content increases the production of H_2 but tends to decrease the production of CO_2 and CH_4.

On the other hand, the influence of the replacement ratio on the gas fraction of the fuel was also analysed. At 900 °C and considering a ratio of 1% MBM, the gas fraction increases from 3.18 m^3/kg$_{ash}$ (STP) to 4.47 m^3/kg$_{ash}$ (STP), but the gas energy yield decreases by 24.1%. This decrease is the result of the decline in the lower heating value (LHV) of the gases, from 3.36 MJ/m^3 (STP) to 2.16 MJ/m^3 (STP). However, it is demonstrated that an increase in the temperature will cause the gas energy yield to increase.

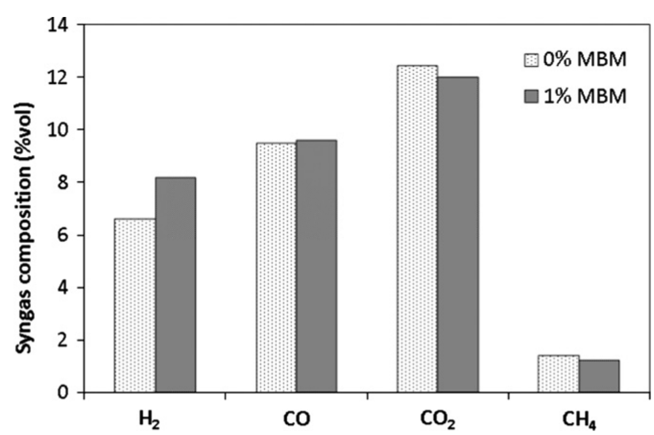


Fig. 5. Comparison of gas compositions from the coal gasification process and MBM-coal co-gasification at 800 °C. Data obtained from [68].

Although MBM has been considered as an alternative fuel in the cement industry, its use as raw material has not. Actually, there are very few references concerning this topic in literature.

In spite of the lack of environmental analysis of the use of MBM as a raw material, Colling [70] conducted one of the first studies concerning the feasibility of producing concrete products from MBM ash.

After that study, Deydier et al. [71] proposed new valorisation techniques including the use of raw material in the cement

Table 11
Quality of RDFs from household and industrial sources. Data obtained from [110].

	Calorific value MJ/kg	Ash residual wt%	Cl content wt%	S content wt%	Water content wt%
Household waste	12–16	15–20	0.5–1		10–35
Household	13–16	5–10	0.3–1	0.1–0.2	25–35
Commercial waste	16–20	5–7	< 0.1–0.2	< 0.1	10–20
RDF from industrial waste	18–21	10–15	0.2–1		3–10
Demolition waste	14–15	1–5	< 0.1	< 0.1	15–25

Table 12
Chemical analysis of an RDF. Oxygen calculated by difference. Data obtained from [74].

Proximate analysis (wt% dry basis)	
Volatile matter	79.7
Fixed carbon	6.8
Ash	13.5
Ultimate analysis (wt% dry basis)	
C	48.8
H	7.8
N	0.7
S	0.0
O	29.2
HHV (MJ/kg)	19.9

Table 13
Syngas characteristics from RDF gasification. Data obtained from [74].

Properties	
Density (kg/m^3)	0.79
Gas production (m^3/kg)	1.03
Heating value (MJ/m^3)	17.8
Energy content (MJ/kg)	18.33
Components	
O_2 (m^3/kg)	0.0
H_2 (m^3/kg)	0.44
CO (m^3/kg)	0.16
CO_2 (m^3/kg)	0.18
CH_4 (m^3/kg)	0.18
C_2H_4 (m^3/kg)	0.06
C_2H_6 (m^3/kg)	0.0
C_3 (m^3/kg)	0.0
Tot (m^3/kg)	1.03
H_2/CO	2.7

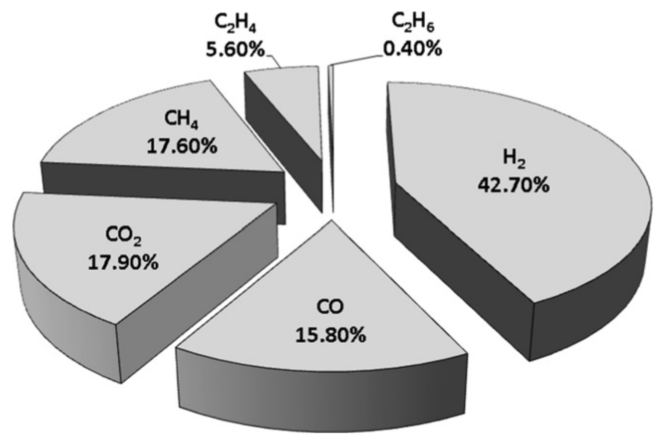


Fig. 6. Composition of syngas from RDF gasification. Data obtained from [74].

industry after analysing the physical and chemical properties of MBM combustion residues. The results demonstrate that MBM ashes mainly consist of compounds rich in Ca (30.7%) and phosphate (56.3%), as well as sodium (Na) (2.7%), potassium (K) (2.5%), and Mg (0.8%), among others, and some of these elements are also natural components of clinker or cement materials.

Cyr and Ludmann [69] extended this point of view and analysed the potential for the use of the low risk MBM bottom ash in mortars as a sand replacement. Although MBM bottom ash has physical properties that are similar to fine sand, this ash has a greater water absorption capacity. This fact limits the proportion of sand replacement to values of approximately 30%. However, only replacement ratios of 17% of MBM ash have achieved compressive strength values that are similar to the mortars without MBM added.

The addition of MBM ash as a raw material was also studied recently in the building sector for applications such as the production of bricks [72] or other ceramic materials [73].

5.2. Municipal solid waste (MSW)

MSW production is increasing notably in Europe, and MSW has become a common alternative fuel in the cement industry. However, most cement plants do not directly burn unsorted MSW due the heterogeneous nature of the waste and the presence of components that could pose quality and environmental concerns.

The RDFs from MSW have different physical and chemical properties depending on their sources, especially with respect to their ash, chlorine, sulphur, and water contents. As evident in Table 11, there are notable differences among RDFs, and certain physical and chemical properties can cause difficulties in the kiln combustion process in cases where the RDF is introduced directly. An alternative to the direct introduction of an RDF is to homogenise the fuel by gasification. Obviously, the properties of the final syngas will depend on the characteristics of the RDF, but the producer gas has a uniform composition.

Galvagno et al. [74] performed a study using RDF as an alternative fuel. In this study, the RDF was subjected to gasification processes. The main physical properties of the raw material are represented in Table 12.

These experimental tests indicate a high conversion ratio (close to 86%) of the RDF into producer gas. The main characteristics of the syngas produced are given in Table 13, and the composition of the syngas is presented in Fig. 6. With respect to the suitable exploitation of the syngas, the heating value obtained is similar to that of the RDF raw material. Rovira et al. [75] carried out a study to analyse the effects of increasing the substitution ratio of an RDF in a conventional fuel up to 20% on the PCDD/Fs levels and the concentrations of several metals in monitored areas such as the soil, vegetation, and air. The RDF mixture was formed by plastics (35%), paper, and cartons (30%), wood (20%), and textiles (15%). The feeding material consisted of RDF and petcoke and had a calorific value of approximately 3750 kcal/kg. Tables 14 and 15 lists the emission levels of pollutants from the stack of the cement plant when operating on only the traditional petcoke fuel and after the replacement of 15% of the petcoke with the RDF.

The environmental monitoring demonstrates that the levels of PCDD/Fs and metals surrounding the cement plant are similar for both of the cases compared (only petcoke as fuel and fuel with a replacement ratio of 15% RDF). The particulate matter values are similar for both scenarios, and significant reductions occur for

Table 14
Emission levels of minor pollutants from the stack of a cement plant before (0%) and after (15%) the partial substitution of fossil fuel with an RDF. Data obtained from [75].

	Unit	Sustitution rate		Emission limit
		0 (%)	**15** (%)	
HCl	mg/N/m^3	1.3	1.3	10
HF	mg/N/m^3	0.03	0.03	1
Cd	mg/N/m^3	< 0.0079	< 0.0101	
Ti	mg/N/m^3	< 0.0097	0.0039	
Cd+Ti	mg/N/m^3		0.0039	0.05
Sb	mg/N/m^3	< 0.0097	< 0.0121	
As	mg/N/m^3	< 0.0097	< 0.0121	
Pb	mg/N/m^3	< 0.0079	< 0.0101	
Cr	mg/N/m^3	< 0.0079	< 0.0101	
Co	mg/N/m^3	< 0.0079	< 0.0101	
Cu	mg/N/m^3	0.0021	0.0033	
Mn	mg/N/m^3	0.0029	0.005	
Ni	mg/N/m^3	< 0.0079	< 0.0101	
V	mg/N/m^3	< 0.0097	< 0.0121	
Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V	mg/N/m^3	0.005	0.0083	0.5
Hg	mg/N/m^3	0.0085	0.0094	0.05
PCDD/Fs	ngI-TEQ/N/m^3	0.00143	0.0032	0.1

Table 15
Environmental comparison of metals and PCDD/Fs in vegetation samples collected around the cement plant before (2008) and after (2009) the partial substitution of fossil fuel with an RDF. Data obtained from [75].

	Units	2008	2009	% 2008–2009
As	mg/kg	0.08	< 0.10	–
Cd	mg/kg	0.06	0.05	−24
Co	mg/kg	0.50	0.04	−1299
Cr	mg/kg	2.87	1.00	−188
Cu	mg/kg	5.58	5.30	−5
Hg	mg/kg	< 0.10	< 0.10	–
Mn	mg/kg	40.9	30.0	−37
Ni	mg/kg	1.79	0.78	−128
Pb	mg/kg	0.46	0.13	−243
Sb	mg/kg	0.06	< 0.10	–
Sn	mg/kg	0.11	0.07	−60
Tl	mg/kg	0.01	0.15	90
V	mg/kg	< 0.25	< 0.25	–
Zn	mg/kg	30.7	21.6	−42
2,3,7,8-TCDD	ng/kg	0.01	< 0.01	–
1,2,3,7,8-PeCDD	ng/kg	< 0.03	< 0.03	–
1,2,3,4,7,8-HxCDD	ng/kg	0.01	< 0.03	–
1,2,3,6,7,8-HxCDD	ng/kg	0.02	0.02	5
1,2,3,7,8,9-HxCDD	ng/kg	0.02	< 0.03	−22
1,2,3,4,6,7,8-HpCDD	ng/kg	0.17	0.13	−35
OCDD	ng/kg	0.95	0.49	−94
2,3,7,8-TCDF	ng/kg	0.06	0.05	−23
1,2,3,7,8-PeCDF	ng/kg	0.04	0.05	18
2,3,4,7,8-PeCDF	ng/kg	0.05	0.03	−61
1,2,3,4,7,8-HxCDF	ng/kg	0.04	0.04	19
1,2,3,6,7,8-HxCDF	ng/kg	0.04	0.04	17
1,2,3,7,8,9-HxCDF	ng/kg	< 0.03	< 0.03	–
2,3,4,6,7,8-HxCDF	ng/kg	0.04	0.02	−89
1,2,3,4,6,7,8-HpCDF	ng/kg	0.14	0.25	44
1,2,3,4,7,8,9-HpCDF	ng/kg	< 0.05	< 0.05	–
OCDF	ng/kg	0.10	0.57	82
Total WHO-TEQ	ng/kg	0.09	0.06	−61

a number of pollutants (PCDD/Fs, Co, Cr, Mn, and Ni) in the vegetation, as well as in the soil (Ni) and the air (Sn). These results indicate that alternative fuels formed by MSW materials may be a viable choice to replace a portion of classical fossil fuel use.

When MSW is used as a raw material in cement or mortar production, the heterogeneity of the mixtures again becomes one of the most significant problems. Normally, the ashes produced during combustion or incineration processes are introduced into the process to partially replace some of the natural raw materials that are used.

It was demonstrated that the addition of a controlled amount of MSW ash in cement and mortar is suitable in terms of the MSW shrinkage and mass loss properties. The formation of hydrated materials due to the high chloride and sulphate content in MSW fly ash may result in an increased immobilisation of water [76]. In regard to the compressive strength, it was demonstrated experimentally that there is not a remarkable difference even when replacement ratios of MSW up to 10% are used [77].

Other important parameters to characterise in these mixtures are the flow and the initial and final setting times. Krammart et al. [78] performed several experiments with replacement ratios of 0, 5, and 10% of MSW. The results indicate that the initial and final setting times increase and the flow rate decreases when the MSW replacement ratio is increased.

On the other hand, the ash contains valuable components that allow for the conservation of natural raw materials during the process of cement production. Approximately 90% of the bottom ash consists of grate ashes, which consist of glass, ceramics, ferrous, and nonferrous metals and minerals (i.e., the bottom ash is mainly SiO_2, Ca, or iron (Fe)). The bottom ash also contains a high soluble fraction that mainly consists of chlorides and sulphates. Nevertheless, heavy metals such as lead (Pb) and cadmium (Cd), and PCDD/Fs are also found in high levels in the ash [77].

In further regards to MSW ash, Saikia et al. [79] observed that although $CaCO_3$ and small amounts of SiO_2 and Fe_2O_3 are introduced into cement clinkers during manufacturing, the addition of amounts of MSW fly ash above 44% to the mixture can save approximately 20% of the conventional amount of $CaCO_3$ required in cement production. This reduction represents a significant decrease in the emissions of CO_2.

5.3. *Sewage sludge (SS)*

SS has a high water content. This is an important aspect to be considered when SS is used in gasification and, especially, in combustion processes. In general, the SS is dried before being used as an alternative fuel or raw material and the cost of this process is important. Normally, SS is dried using the waste heat from the cement kiln. Then, it is placed in the main furnace of the cement kiln and burned as a fuel, or it is gasified beforehand and the gas produced is used as an alternative fuel in cement

kilns, heaters, or pre-calciners. In both cases, the residual non-combustible components of the sludge are used as raw materials in cement production.

Related to this topic, Xie et al. [80] conducted a study to determine the influence of the moisture content of SS on air gasification (in a downdraft fixed-bed) under a stable air flux of 0.05 m^3/h and a constant gasification temperature of 800 °C.

As evident in Figs. 7 and 8, increasing the moisture content from 0 to 52.9% causes an increase in the CO_2, H_2, and CH_4 contents in the gas producer and its LHV, from 8.68%, 16.27%, 6.14%, and 6324 kJ/m^3 to 12.25, 18.12, 9.20%, and 6965 kJ/m^3, respectively, while the content of CO decreases from 18.79 to 13.62%. On the other hand, the tar yield from the gasification process decreases with an increase in the moisture content of the raw SS. Additionally, the tar is mainly produced by the pyrolysis of the sludge in the pyrolysis zone; therefore, if the volatile content in the sludge is high, then a high tar volume is produced under the same gasification conditions. In conclusion, increasing the moisture content in the sludge can improve the gas quality, while the yield of the aqueous phase is reduced.

On the other hand, it is also important to consider the gasification technology. Under the premise supported by Li et al. [81], the temperature is the most important factor in gasification process and higher temperatures contribute to higher H_2 production and syngas yields. However, considering the decrease in the heating value, Nipattummakul et al. [82] recently performed an experiment that demonstrates that steam gasification, which creates higher temperatures than air gasification, is more efficient than pyrolysis for the treatment of SS. This latter study demonstrates that the steam technology produces a higher percentage of H_2 in the syngas, which is the result of the higher working temperature, as evident in Fig. 9. Although, the H_2 syngas yields from gasification and pyrolysis increase when the temperature is increased, SS gasification by steam generated approximately three fold more H_2 than that generated by air gasification. Additionally, the syngas quality is evaluated in Fig. 10. The qualitative behaviour of the components is similar for both cases. Only the H_2 and CO concentrations generated increase as a function of the temperature. However, in quantitative terms, the CH_4, hydrocarbon, and CO mole fractions generated by the gasification process are

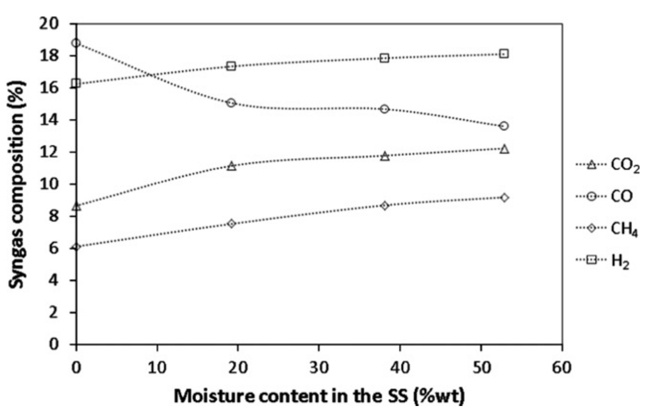


Fig. 7. Effect of moisture content of sludge on the composition of syngas. Data obtained from [80].

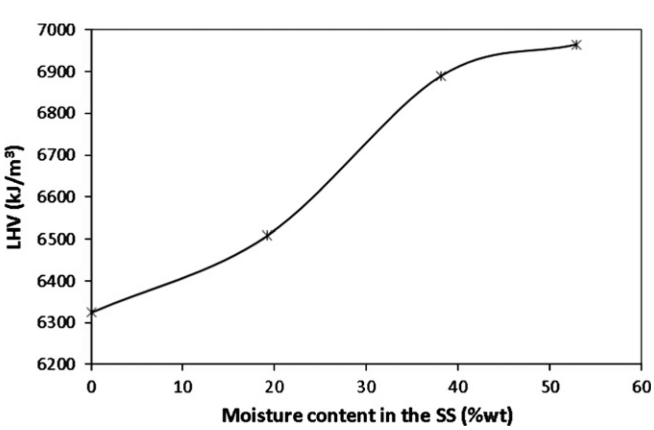


Fig. 8. Effect of moisture content of sludge on the LHV of a gas. Data obtained from [80].

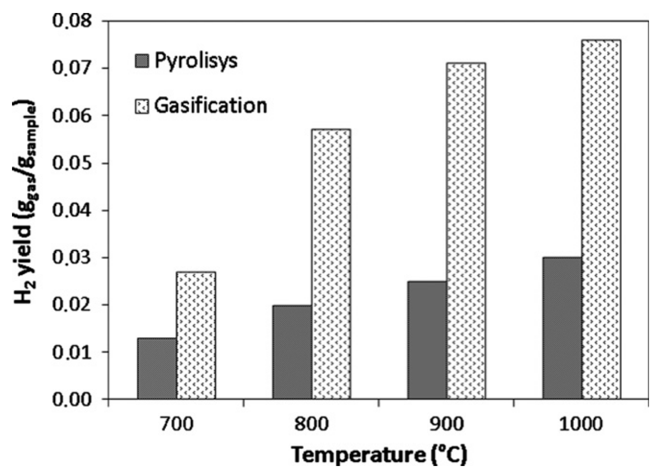


Fig. 9. Hydrogen yield generated by gasification and pyrolysis processes at 700, 800, 900, and 1000 °C. Data obtained from [82].

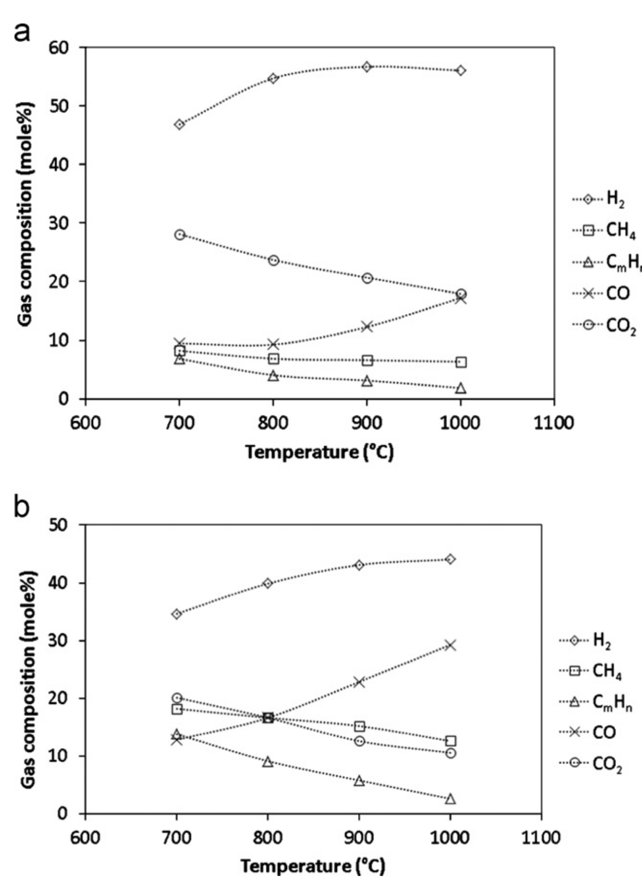


Fig. 10. Syngas composition at 700, 800, 900 and 1000 °C from different processes: (a) gasification and (b) pyrolysis. Data obtained from [82].

lower than those generated by pyrolysis, while the H_2 and CO_2 mole fractions are higher.

In the case of direct combustion into the kiln, the SS moisture content is one of the more important factors to be considered. In this case (when there is no prior production of an energy-rich syngas), the moisture content has a negative effect on the combustion process that is associated with the heat loss due to water evaporation (2257 kJ/kg_{water}), which reduces the net amount of energy released during sludge combustion. This negative impact contributes to an inefficient auto-thermal combustion process, and supplementary fuel must be supplied to overcome the heat losses generated from the heating and evaporation of the water content of the SS, as evident in Table 2, and to maintain the required combustion conditions.

In addition to the moisture content (dryness) of the sludge, other important parameters may potentially affect the overall combustion process of SS, such as the release and combustion of volatile compounds and the combustion of the high ash content remaining as char or slag. Fytili and Zabaniotou [83] considered that wet SS should have a maximum moisture content of 80 wt%, 50 wt% of ash (dry mass), 90 wt% of volatile compounds (dry and ash-free mass), and a fixed carbon content less than 10 wt%. However, lower moisture values of 20% are more desirable as is demonstrated by Aranda-Usón et al. [1] also from the environmental point of view by means of an life cycle analysis. The moisture problem can be improved with pre-dried sludges. On the other hand, to control the other factors, some authors [84,85] suggest a maximum SS feed rate of 5% of the clinker production capacity.

Additionally, a recent study conducted by Gálvez et al. [86] showed very promising results regarding the interactions between pollutants produced in SS combustion and cement raw material. The results indicate that the presence of cement raw material at the outlet of the combustion gas is beneficial for decreasing the emissions of polycyclic aromatic compounds (PAH) and PCDD/Fs.

From the point of view of the substitution SS for natural resource raw materials such as limestone in the cement manufacturing process, sludges are a valuable waste resource because of the high contents of Al_2O_3, Fe_2O_3, and SiO_2. Nevertheless, the final compressive strength requirements limit the amount of sludge that can be incorporated as raw material. SS contributes positively to compressive strength at replacements ratios lower than 7% [87].

Heavy metals are also present in sludges and are a problem in terms of sludge management. However, positive results have been achieved in the case of SS additions in cement manufacturing. The concentrations of heavy metals in the clinker are related to their volatility during the burning process. It were demonstrated [87] that the content of some heavy metals such as Cr, Zn, and Ni have no influence on the formation of the clinker phases, the final compressive strength, and the initial setting time or hydration level when their concentrations are below 0.1% in the raw mixture. Additionally, this study found that heavy metals are not detected in the leachates for up to 28 days. This fact is considered as a great advantage to sludge exploitation because the heavy metals are added to the final product and, consequently, the management of final residues with high levels of metals is avoided.

In contrast to dealing with the heavy metal content, one of the obstacles to the introduction of sludges to cement kilns is their relatively high phosphorus pentoxide (P_2O_5) and Cl contents. Because of the influence of P_2O_5 on the clinker phases formation, this substance has an important effect over the final product quality [88]. Increasing the P_2O_5 initial content in the mixture, it is shown an increment in CaO and aluminate, a descent in alite amount, and an instable behaviour in ferrite content in the clinker composition. As a final result, a decrease in the clinker quality is found. However, although chloride causes the opposite effect of P_2O_5, it is concluded that Cl compounds are more relevant to the kiln process than the quality of the clinker.

5.4. Biomass

Biomass is one of the most extensively used alternative materials in the cement industry because of its diversity and volume. The major restrictions to the use of biomass in cement manufacturing are linked to economic factors, the necessity of pre-treatment stages, and the local availability of the resources or the transport costs, which are less restrictive than technical limitations [89].

In general, biomass is defined as any type of organic material, except those which are catalogued as toxic or hazardous by directive 2008/98/CE [13] and those that contain substances such as varnish, paint, or glue.

A wide array of different types of biomass is used in combustion or gasification processes, for example, sawdust or wood [74,90–92], straw [93,94], agriculture and forest wastes [89,93,95], almond shells [96,97], and olive residues [96,98].

In spite of this wide diversity of biomass types, wood and other waste from agriculture and forest processes are some of the most common types of biomass processed by combustion or gasification.

Biomass additions can replace a portion of the traditional fuel use. Although replacement ratios approximately 20% are recommended to maintain a stable combustion process and the quality of the clinker, higher values have been used with very satisfactory results [99].

Ca and K are important components in biomass. Because an increase in the potassium oxide (K_2O) content decreases the melting point of the ashes, enhancing agglomeration problems in the combustion chambers [95], the co-combustion of biomass with coal or petcoke, which have lower calcium contents, is recommended. These mixtures produce ashes with a higher melting point and operational problems are thus avoided. However, an increase in the sulphur, Al, and Fe content of the clinker is observed in comparison that produced by the combustion with pure traditional fuels [92]. Moreover, the alkaline base and chlorine contents are also important, especially at high levels because they can cause deposition, slag fusion, or corrosion problems.

On the other hand, the sulphur and nitrogen contents in biomass are lower than those in coal or petroleum, and therefore, the SO_x and NO_x emissions are also reduced. Moreover, taking into account that the most of the nitrogen in biomass is converted to ammonia, which promotes the conversion of NO_x to gaseous nitrogen, the emissions of NO_x are also reduced [99].

In the case of gasification, there are no restrictions on the replacement ratio, particularly when using wood as an alternative fuel. Galvagno et al. [74] performed an experiment in which the gasification of poplar was carried out. For the heat treatment process, the samples of poplar wood sawdust were dried and milled into particles up to 4 mm in diameter, and maintained at ambient conditions. The main physical properties of the raw material are presented in Table 16. The low nitrogen content in the ash is remarkable.

In this experiment, the gasification process converted over 80% of the poplar raw material into syngas, the main characteristics of which are listed in Table 17. The final gas composition is presented in Table 18. In this case, the producer gas energy content is slightly low, 14.7 MJ/kg, although it is high enough to be used in a cement plant as a secondary fuel.

Table 16
Chemical analysis of poplar. Oxygen calculated by difference. Data obtained from [74].

Proximate analysis (wt% dry basis)	
Volatile matter	81
Fixed carbon	17.3
Ash	1.7
Ultimate analysis (wt% dry basis)	
C	47.5
H	6.1
N	0.1
S	0.0
O	44.6
HHV (MJ/kg)	19.0

Table 17
Syngas characteristics from poplar gasification. Data obtained from [74].

Density (kg/m^3)	0.82
Gas production (m^3/kg)	1.10
Heating value (MJ/m^3)	13.40
Energy content (MJ/kg)	14.70

Table 18
Composition of syngas from poplar gasification. Data obtained from [74].

Component	Composition (%)
H_2	45.5
CO	23.1
CO_2	20.8
CH_4	8.6
C_2H_6	0.1
Steam/biomass ratio	2.2
H_2/CO	2

From the point of view of the use of biomass as an alternative raw material in mortar or concrete manufacturing, biomass ashes also provide an important resource because of their chemical composition, which is based on essential oxide compounds such as SiO_2, Al_2O_3, Fe_2O_3, and quicklime (CaO). The proportion of each component depends on the type of biomass.

Some studies analysed the behaviour of wood as an alternative raw material and the final properties of the mixtures [100–102]. The results show that blending cement with wood ash increases the consistency and soundness values as well as the initial and final setting times. The delay in the setting time becomes more significant with an increase in the level of ash in the mixture. The maximum replacement ratio is established as 30%. Additionally, it is demonstrated that the water requirements for concrete and mortar mixtures containing wood ash are greater to maintain a proper level of workability in the final product [100].

Specifically, Wang and Baxter [101] carried out studies concerning the impacts of adding biomasses fly ashes in the concrete manufacturing process on two key aspects of concrete, its strength and its durability. The experimental results, when replacement ratios of 25% were considered, confirm that biomass fly ash additions produce concrete with at least an equal or even a much better performance with respect to both of these parameters.

In comparison with these results, Maschio et al. [102] also analysed the behaviour of mortars with different replacement ratios of fir chip ashes. In this case, the author suggests a maximum replacement ratio of 5% to maintain a compression strength and absorption level of the same magnitude as those of the reference mortar. On the other hand, the results demonstrate that the contents of KCl and K_2SO_4 are the responsible for the precipitation of gypsum and portlandite during the first hydration stage of the paste formation and, consequently, enhance the apparent viscosity of the mortar.

5.5. End-of-life tyres (ELT)

Tyres are one of the most promising alternatives to the traditional fuels used in the incineration process in the cement industry. The high temperature in a cement kiln ensures the complete destruction of ELTs. Moreover, tyres are one of the most powerful alternative fuels because of their high energy content (above 30 MJ/kg), low degree of material diversification, and low moisture levels, as evident in Table 7.

The technical, environmental and economic viability of using tyres in cement manufacturing processes has been analysed in recent years [27,103–106]. Consequently, it is demonstrated that the amount of coal or petcoke required is reduced and, consequently, the costs associated with their use.

In regards to atmospheric emissions of GHGs and pollutants, it is observed that the CO and total hydrocarbon emissions form the combustion of ELT-fuel mixtures are slightly higher compared to those from non-ELT firing kilns. In contrast, no significant differences are found in the emissions of SO_2, NO_x, total hydrocarbons, CO, and metals [46].

However, tyres have some limitations when they are introduced into the kiln directly because of the large quantity of Zn that remains in the ashes, which can modify the cement composition dramatically. To avoid this problem, replacement ratios under 30% are suggested for the kiln fuel. Pipilikaki et al. [104] carried out experimental studies using a 6% replacement of the total fuel as tyre-derived fuel (TDF). Their results demonstrate that there are only slight variations in the cement setting time and water requirements.

On the other hand, the gasification process is less restricted, and therefore, this option is currently being developed. Galvagno et al. [74] performed a study using scrap tyre samples that were dried and shredded to a 2 mm particle size diameter as an alternative fuel in the gasification process. The main physical properties of the raw material are presented in Table 19. The high content of fixed carbon in the tyres is especially remarkable.

The main characteristics of syngas produced by the gasification process are listed in Table 20, and the composition of the syngas is presented in Fig. 11. With respect to the suitable exploitation of the syngas, the heating value obtained is lower than that of the tyre raw material, although it is extremely high in comparison with the producer gas generated from the other

Table 19
Chemical analysis of scrap tyres. Oxygen calculated by difference. Data obtained from [74].

Proximate analysis (wt% dry basis)	
Volatile matter	61.8
Fixed carbon	33.8
Ash	4.4
Ultimate analysis (wt% dry basis)	
C	85.2
H	7.3
N	0.4
S	2.3
O	0.5
HHV (MJ/kg)	37.1

alternative fuels, such as MBM, SS, RDF, or wood, which have been described in previous sections.

Although the inert parts of tyres can be introduced as raw materials into the cement matrix during the direct combustion process in kilns, the potential for using recycled tyres as a raw material is more focused on using the rubber tyre particles as coarse or fine aggregate in concrete or mortars. Some studies [107,108] were conducted to determine the mechanical properties of tyre mixtures. The flexural strength and the capacity to mitigate moisture damage are increased when rubber tyre particles are introduced into the manufacturing process. Regarding the increase in flexural strength, the crack widths in rubberised concrete are minimised and the propagation of symptoms of failure are more uniform and gradual. Other important aspects to consider include the improvements in thermal isolation, sound absorption, and material durability. However, other analyses demonstrate a remarkable decline in the compressive and tensile strength as well as the density of the cement. Due to the considerable decrease in the final compressive strength, rubber concentrations exceeding 25% are not recommended [107]. To mitigate this phenomenon, Pelisser et al. [108] proposed a chemical treatment by sodium hydroxide followed by the addition of 15% silica fume. The results indicate a recovery in compressive strength up to the values obtained for concrete samples without any tyres particles included in their composition.

Table 20
Characteristics of syngas generated from the gasification of tyres. Data obtained from [74].

Properties	
Density (kg/m^3)	0.55
Gas production (m^3/kg)	1.09
Heating value (MJ/m^3)	25.33
Energy content (MJ/kg)	28.12
Components	
O_2 (m^3/kg)	0.02
H_2 (m^3/kg)	0.55
CO (m^3/kg)	0.07
CO_2 (m^3/kg)	0.05
CH_4 (m^3/kg)	0.29
C_2H_4 (m^3/kg)	0.1
C_2H_6 (m^3/kg)	0.01
C_3 (m^3/kg)	0.01
Tot (m^3/kg)	1.09
H_2/CO	7.8

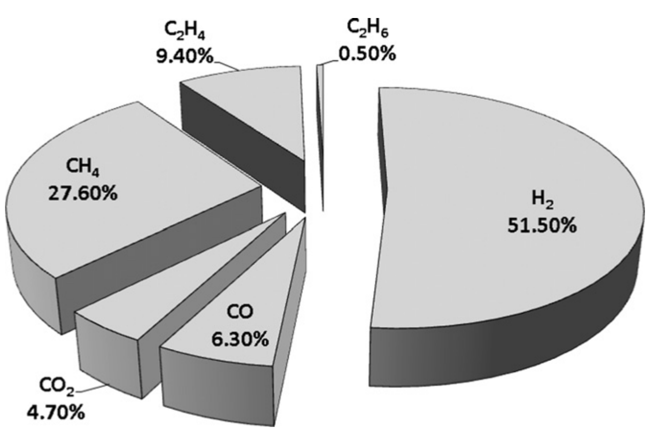


Fig. 11. Composition of syngas from tyre gasification. Data obtained from [74].

On the other hand, technological developments have also improved the quality of concrete and rubber mixtures. In this regard, self-compacting technology appears to be a suitable option for obtaining mixtures with more versatile mechanical properties. Bignozzi and Sandrolini[109] showed that the use of self-compacting technology helps bind rubber phases, and this technology allows the producer to maximise the amount of rubber tyre wastes used in the manufacturing process.

6. Conclusions

The cement industry is an energy-intensive and high pollutant emitting industry. Although several improvements in cement technologies and equipment have been developed, there is a high potential to reduce the consumption of non-renewable fossil fuels for energy, which is also one of the main sources of emissions, by replacing them with alternative fuels. In terms of the diversity of available alternative fuels, the cement industry presents the opportunity to recover the energy from several waste materials under optimal technical and environmental conditions, avoiding losses of energy to processes associated with the waste management chain, such as incineration or landfilling. Fig. 12 presents this approach graphically. By coupling the cement and waste management industries, it is possible to significantly reduce the GHG emissions and natural resource consumption associated with cement production. Therefore, the replacement of fossil fuels and natural materials with alternative materials is not only an environmentally friendly method of waste management but also a cost saving and suitable way to conserve fossil fuels and natural resources.

This study provides a practical analysis of the influence of the use of alternative materials in the cement industry, taking into account previously published research studies. Alternative fuels can be introduced into the cement manufacturing process in two different ways, by direct combustion or by following a gasification phase with the combustion of the producer gas in the cement

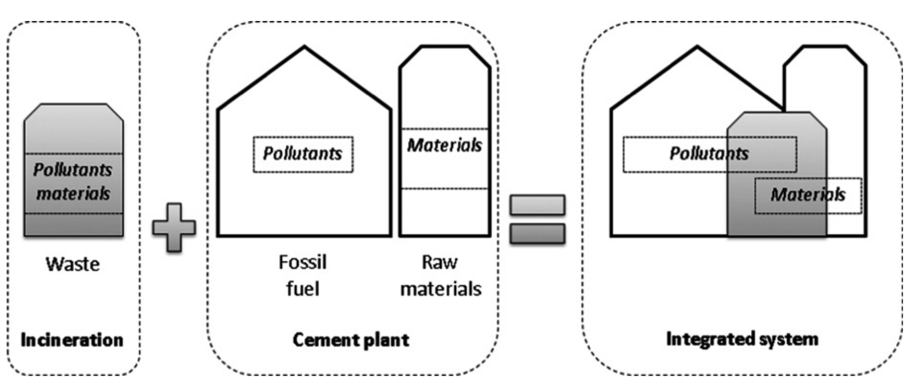


Fig. 12. Reduction of the combustion emissions and raw material use by linking the waste treatment and cement industries. Adapted from [3].

production process. In both cases, specific considerations regarding regulatory requirements must be observed.

The final energy content of the feed fuel depends on the nature and state of the raw material. In the case of direct combustion, the energy content refers directly to the original alternative fuel. In this case, only tyres have a heating value that is similar or even higher than those of traditional fuels. However, if the alternative fuel is subjected to a gasification process, the energy content of the producer gas differs from that of the original alternative fuel. The final H_2 composition in the producer gas establishes the energy content of the fuel. This fact is affected not only by the nature of the alternative fuel but also by the gasification technology applied and the associated conditions.

Nevertheless, special efforts have been taken to analyse the alternative fuel gasification process because this is the technical route that allows more flexibility and less impact in the use of secondary fuels in the kiln, pre-heaters, and pre-calciners. The syngas obtained from the gasification process and used as fuel in the cement industry has a homogeneous composition and, hence, its combustion in the kilns is easier to manage. On the other hand, taking into account that the gasification process is an external process to the cement kiln, this technology allows the produce to have greater control over the addition of slag as raw material into the cement production process. Accordingly, the composition and quantity of the slag depends on the alternative fuel that is used and the final cement requirements; however, it is possible to properly control the material fed into the kiln.

On the contrary, wastes used as alternative raw materials are usually added in form of ashes. The conversion to ash can be performed directly in the kiln when the alternative material is introduced as a fuel or can be performed in an external device and introduced, for example, as a residue of a gasification or an incineration process. Wastes can be used an alternative raw material in the clinker formation process, in cement manufacturing, or in concrete production.

The quality of the final product is one of the most important considerations to be taken into account when wastes are added as raw materials. Properties such as the initial and final setting times, the leachability, the compressive and tensile strengths, the mitigation of moisture damage, and the durability have been considered extensively in recent research studies. Although different results are found depending on the type of alternative material examined, this research supports and reinforces the suitability of the use of several waste materials as alternative resources or raw materials in the cement industry.

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